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Energetics of HF Elimination and N–F Bond Cleavage in Some Difluoramines and *Gem*-Nitro/Difluoramines

by

Peter Politzer, Pat Lane, and M. Edward Grice

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Department of Chemistry
University of New Orleans
New Orleans, LA 70148

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13. ABSTRACT (Maximum 200 words)

We have shown, through density functional calculations (Becke exchange/Lee, Yang and Parr correlation functionals, 6-31G** basis set) that the elimination of HF from H_3C-NF_2 is thermodynamically favored, $\Delta G(298.15\ K) = -29$ kcal/mole, but has a relatively high activation barrier, $\Delta G^{\ddagger}(298.15\ K) = 38$ kcal/mole. The N–F dissociation energy, ΔE_{N-F}, is found to be 69 kcal/mole. Introduction of a nitro group, giving $H_2C(NO_2)NF_2$, produces only small changes in these values: $\Delta G(298.15\ K) = -28$ kcal/mole; $\Delta G^{\ddagger}(298.15\ K) = 36$ kcal/mole; $\Delta E_{N-F} = 66$ kcal/mole. Replacement of all *alpha* hydrogens by methyl groups increases the N–F dissociation energies slightly (<2 kcal/mole). These substituent effects are interpreted in terms of geminal interactions.

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## Introduction

There is a continuing interest in the difluoramino group, $-NF_2$, as a potentially important substituent in energetic systems, particularly propellants [1-6]. As is discussed elsewhere, replacing some $-NO_2$ groups by $-NF_2$ can increase the number of moles of gaseous combustion products formed per gram of material [5, 7], thereby enhancing propellant performance [5, 8]. A number of mixed nitro/difluoramino derivatives have been synthesized [2, 3, 9], including compounds in which the two groups are on the same carbon, *gem*-nitro/difluoramines [10].

A source of concern when a difluoramine contains an *alpha* hydrogen is instability with respect to loss of HF [11, 12]:

$$R_2\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle F}{|}}{N}-F \longrightarrow R_2C{=}N{-}F \ + \ HF \tag{1}$$
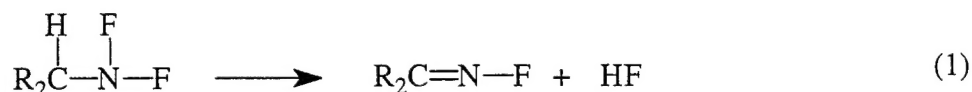
An analogous possibility exists in the case of hypofluorites [13-15], in which fluorine is also bonded to a highly electronegative atom, in this case oxygen:

$$R_2\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle F}{|}}{O} \longrightarrow R_2C{=}O \ + \ HF \tag{2}$$
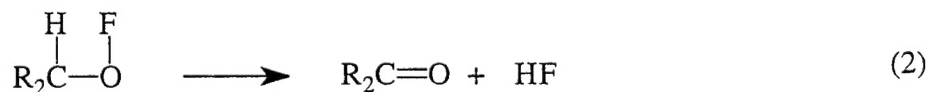
Indeed reaction (2) is apparently more likely than (1), which requires a catalyst [11, 12]. However H_3C-OF has been isolated and characterized [13-15], and its unimolecular decomposition to $H_2C{=}O$ and HF has been subjected to a detailed computational analysis [16]. The two most favorable (and possibly competing) pathways were found to be (a) a single-step HF elimination through a four-centered transition state, and (b) a two-step process involving an initial, and rate-determining, cleavage of the O–F bond. While the overall reaction,

$$H_3C{-}OF \longrightarrow H_2C{=}O \ + \ HF \tag{3}$$
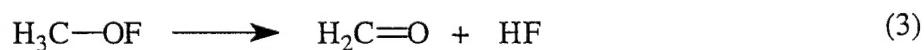
was predicted to have a strong thermodynamic driving force, $\Delta E = -73.9$ kcal/mole at the correlated *ab initio* G2 level [16], the relatively high free energies of activation (>36 kcal/mole at 300 K) obtained for both of the pathways described above indicate an unexpected level of kinetic stability for H_3C-OF, as has indeed been observed [13].

Our present objective is to examine various aspects of the elimination of HF from H_3C-NF_2, and how this is affected by the presence of NO_2 on the same carbon. In order to have a more complete picture of the factors influencing the stabilities of difluoramines and *gem*-nitro/difluoramines, our analysis also includes molecules in which there is no *alpha* hydrogen, i.e. $(H_3C)_3C-NF_2$ and $(H_3C)_2C(NO_2)NF_2$.

Methods

Optimized geometries, energies, vibrational frequencies and entropies for all systems of interest were computed with the GAUSSIAN 94 program [17]. A nonlocal density functional procedure was used, involving the Becke exchange [18] and Lee, Yang and Parr correlation [19] functionals, and a 6-31G** basis set. The calculated vibrational frequencies provided verification that all computed geometries correspond either to true energy minima or to transition states, as desired [20]. All energetic data to be given in this paper include zero-point corrections.
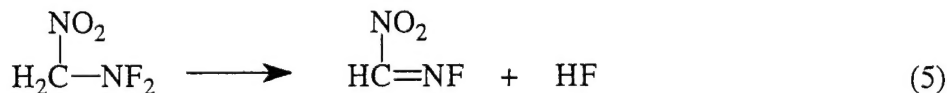
Results and Discussion

Reaction energetics

The loss of HF from either H_3C-NF_2 or $H_2C(NO_2)NF_2$ is found to be thermodynamically favored:

$$H_3C-NF_2 \longrightarrow H_2C=NF + HF \tag{4}$$
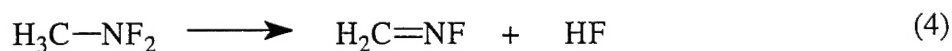
$$\Delta E \ (0 \ K) = -20.1 \ kcal/mole$$
$$\Delta G \ (298.15 \ K) = -28.9 \ kcal/mole$$

$$\overset{\displaystyle NO_2}{\underset{\displaystyle H_2C-NF_2}{|}} \longrightarrow \overset{\displaystyle NO_2}{\underset{\displaystyle HC=NF}{|}} + HF \tag{5}$$

$$\Delta E \ (0 \ K) = -19.4 \ kcal/mole$$
$$\Delta G \ (298.15 \ K) = -28.2 \ kcal/mole$$

As pointed out earlier, the *ab initio* G2 ΔE for the elimination of HF from H_3C-OF is much larger in magnitude, -73.9 kcal/mole [16].

Guided by the results of the H_3C-OF study, we have examined two possible decomposition mechanisms for H_3C-NF_2 and $H_2C(NO_2)NF_2$; the first is one in which they pass through a four-centered transition state and then proceed to lose HF, eqs. (6) and (7),

$$H_3C-NF_2 \longrightarrow \overset{\displaystyle H--F}{\underset{\displaystyle H_2C-NF}{| \quad |}} \longrightarrow H_2C=NF + HF \tag{6}$$
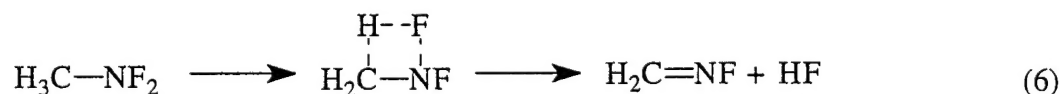
$$\Delta E^{\ddagger} \ (0 \ K) = 38.0 \ kcal/mole$$
$$\Delta G^{\ddagger} \ (298.15 \ K) = 37.9 \ kcal/mole$$

$$H_2C-NF_2 \longrightarrow \overset{H--F}{\underset{NO_2}{HC--NF}} \longrightarrow HC{=}NF + HF \qquad (7)$$
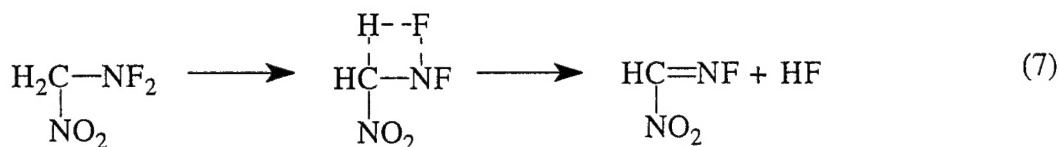
$$\Delta E^{\ddagger} \ (0 \ K) \ = \ 35.2 \ kcal/mole$$
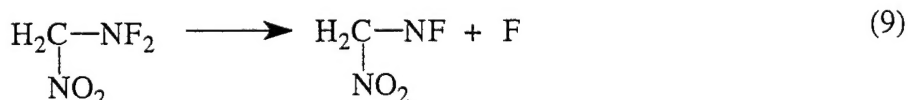$$\Delta G^{\ddagger} \ (298.15 \ K) = 35.7 \ kcal/mole$$

while the second begins with the homolytic cleavage of an N–F bond, eqs. (8) and (9).

$$H_3C-NF_2 \longrightarrow H_3C-NF + F \qquad (8)$$
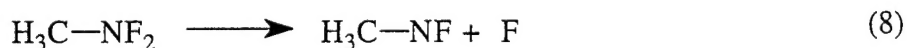
$$\Delta E \ (0 \ K) \ = \ 69.3 \ kcal/mole$$
$$\Delta G \ (298.15 \ K) = 60.6 \ kcal/mole$$

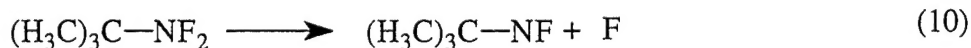$$\underset{NO_2}{H_2C-NF_2} \longrightarrow \underset{NO_2}{H_2C-NF} + F \qquad (9)$$

$$\Delta E \ (0 \ K) \ = \ 65.7 \ kcal/mole$$
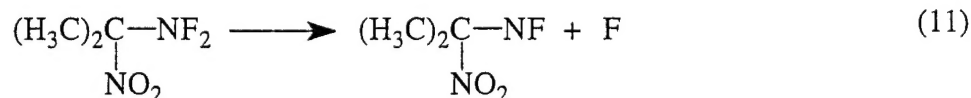$$\Delta G \ (298.15 \ K) = 56.4 \ kcal/mole$$

It is clear that breaking an N–F bond requires more energy, or free energy, than formation of the four-centered transition state; thus the latter is the favored pathway for elimination of HF from either H_3C-NF_2 or $H_2C(NO_2)NF_2$. This conclusion is in contrast to that reached for H_3C-OF [16], in which case the two pathways are competitive in terms of their free energy requirements. The calculated free energies of activation for forming the four-centered transition states are actually quite similar for all three molecules, between 35 and 39 kcal/mole; however the computed O–F bond dissociation energy is considerably less (45.9 kcal/mole [16]) than the N–F in either H_3C-NF_2 or $H_2C(NO_2)NF_2$, and the inclusion of TΔS makes O–F bond-breaking a viable alternative to formation of the transition state. Our values for the N–F dissociation energies, 69.3 and 65.7 kcal/mole, are in very good agreement with other calculated and relevant experimental data [10, 21].

While the presence of the strongly electron-withdrawing $-NO_2$ group might be expected to significantly affect the energetics of processes related to the elimination of HF, we find only a relatively small lowering (≤ 4 kcal/mole) of the energy requirements for either the four-centered transition state or cleavage of an N–F bond. We also examined the consequences of eliminating all

alpha hydrogens and introducing a carbon chain. The N–F dissociation energy is found to increase slightly (< 2 kcal/mole), eqs. (10) and (11):

$$(H_3C)_3C{-}NF_2 \longrightarrow (H_3C)_3C{-}NF + F \qquad (10)$$

$$\Delta E\ (0\ K)\ =\ 71.2\ kcal/mole$$

$$\underset{\displaystyle NO_2}{(H_3C)_2C}{-}NF_2 \longrightarrow \underset{\displaystyle NO_2}{(H_3C)_2C}{-}NF + F \qquad (11)$$
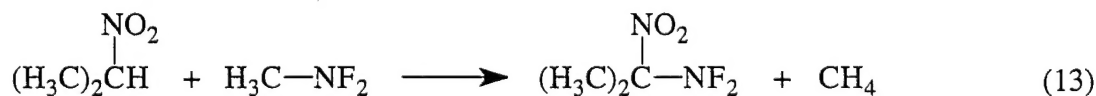
$$\Delta E\ (0\ K)\ =\ 66.8\ kcal/mole$$

Substituent interactions

It is known that two functional groups attached to the same atom can have either a stabilizing or destabilizing interaction, the so-called "geminal effect" [20, 22]. If both groups are overall electron-withdrawing, as are $-NO_2$ [23] and $-NF_2$ [7, 24], then destabilization is anticipated [22]. A commonly used procedure for quantifying this is by means of an appropriate isodesmic reaction [20]. This is a hypothetical chemical process in which the number of bonds of each formal type remains the same but their mutual relationships are changed. The value of ΔE for such a reaction reveals any deviations from bond energy additivity, and is interpreted as reflecting any special energetic effects. Thus, the positive ΔE that we obtain for eq. (12) confirms that the interaction between $-NO_2$ and $-NF_2$, when substituted on the same carbon, is indeed destabilizing:
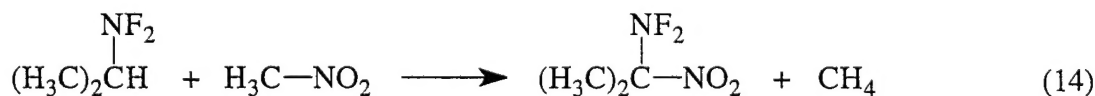
$$H_3C{-}NO_2\ +\ H_3C{-}NF_2 \longrightarrow \underset{\displaystyle NF_2}{\overset{\displaystyle NO_2}{H_2C}}\ +\ CH_4 \qquad (12)$$
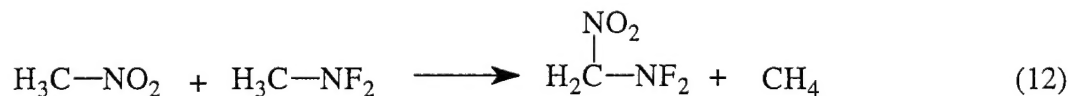
$$\Delta E\ (0\ K)\ =\ 3.5\ kcal$$

However this is countered by the presence of methyl groups:

$$\underset{\displaystyle (H_3C)_2CH}{\overset{\displaystyle NO_2}{}}\ +\ H_3C{-}NF_2 \longrightarrow \underset{\displaystyle (H_3C)_2C}{\overset{\displaystyle NO_2}{}}{-}NF_2\ +\ CH_4 \qquad (13)$$

$$\Delta E\ (0\ K)\ =\ -1.2\ kcal$$

$$\underset{\displaystyle (H_3C)_2CH}{\overset{\displaystyle NF_2}{}}\ +\ H_3C{-}NO_2 \longrightarrow \underset{\displaystyle (H_3C)_2C}{\overset{\displaystyle NF_2}{}}{-}NO_2\ +\ CH_4 \qquad (14)$$

$$\Delta E \ (0 \ K) \ = \ -1.7 \ kcal$$

$$\overset{\displaystyle NO_2}{\underset{\displaystyle |}{H_3C-CH-NF_2}} \ + \ C_2H_6 \ \longrightarrow \ \overset{\displaystyle NO_2}{\underset{\displaystyle |}{(H_3C)_2C-NF_2}} \ + \ CH_4 \qquad (15)$$
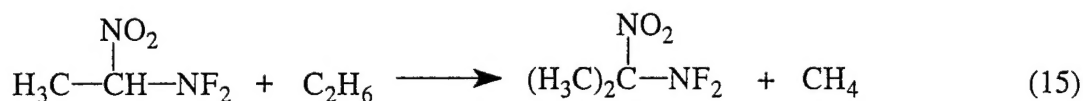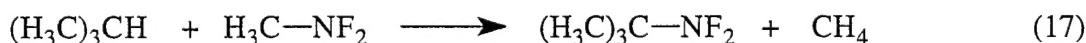
$$\Delta E \ (0 \ K) \ = \ -6.8 \ kcal$$

Stabilization is also observed for just the methyl/difluoramino combination:

$$\overset{\displaystyle NF_2}{\underset{\displaystyle |}{(H_3C)_2CH}} \ + \ C_2H_6 \ \longrightarrow \ (H_3C)_3C-NF_2 \ + \ CH_4 \qquad (16)$$

$$\Delta E \ (0 \ K) \ = \ -4.1 \ kcal$$

$$(H_3C)_3CH \ + \ H_3C-NF_2 \ \longrightarrow \ (H_3C)_3C-NF_2 \ + \ CH_4 \qquad (17)$$
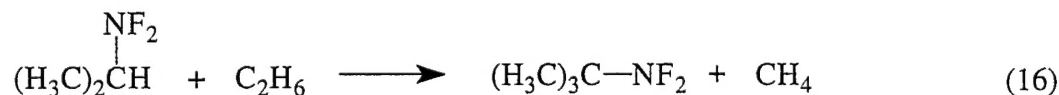
$$\Delta E \ (0 \ K) \ = \ -9.1 \ kcal$$

It was pointed out above that the nitro group slightly lowers the energy requirement for N–F bond cleavage, while the methyl does the opposite. It seems reasonable to suggest that these effects may reflect the destabilizing interaction between geminal difluoramino and nitro groups, and the stabilizing influence of the methyl.

Conclusions

The major points to come out of this work are the following:

(1)   The loss of HF from H_3C-NF_2 is believed to proceed through a four-centered transition state, not via initial rupture of an N–F bond. The activation barrier is relatively high, about 38 kcal/mole. This provides a degree of kinetic stability, even though the elimination of HF is thermodynamically favored: $\Delta G \ (298.15 \ K) = -29$ kcal/mole.

(2)   The above conclusions are only slightly affected by the additional presence of the nitro group on the substituted carbon, $H_2C(NO_2)NF_2$. The activation barrier is reduced by less than 3 kcal/mole, and the overall $\Delta G \ (298.15 \ K)$ is -28 kcal/mole. There is also little change in the N–F dissociation energy, $\Delta E \ (0 \ K)$, which decreases from 69 kcal/mole for H_3C-NF_2 to 66 kcal/mole for $H_2C(NO_2)NF_2$. ˙

(3) When all *alpha* hydrogens are replaced by methyl groups, these N–F dissociation energies increase very slightly (< 2 kcal/mole).

(4) There is a weakly destabilizing interaction between –NF$_2$ and –NO$_2$ when on the same carbon, and a weakly stabilizing one between –NF$_2$ and –CH$_3$. These help to explain the effects, noted above, of nitro and methyl substituents.

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